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(74) Agent: WESEMAN, Steve; CTS Wireless Components, 171 Covington Drive, Bloomingdale, IL 60108 (US).

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(71) Applicant: CTS CORPORATION [US/US]; 905 West Boulevard North, Elkhart, IN 46514 (US).

(72) Inventors: DAI, Xunhu; 1225 E. Lighthouse Circle, Gilbert, AZ 85234 (US). FORST, Donald; 8309 San Francisco NE, Albuquerque, NM 87109 (US).



WO 01/21548 A1

(54) Title: PIEZOELECTRIC CERAMIC COMPOSITIONS AND METHODS FOR PRODUCTION THEREOF

(57) Abstract: Low loss piezoelectric ceramic compositions cofirable with silver at a reduced sintering temperature and methods for producing the such compositions are provided. The compositions are binary piezoelectric ceramic compositions having a first component which is characterized by about 95.0 to about 99.5 weight percent of a system represented by general formula $Pb(Zr_xTi_{1-x})O_3 + y \text{ wt\% MnO}_2$ in which x and y represent weight percentages and wherein x is within a range from 0.0 to about 1.0, and y is within a range from about 0.1 to about 1.0. The compositions also have 0.5 to 5.0 wt% of a second component represented by the general formula $w \text{ wt\% Bi}_2O_3 - z \text{ wt\% CdO}$ in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0. The piezoelectric ceramic compositions are non-reactive with a silver electrode layer when cofired therewith at sintering temperatures of about 900 °C and may be employed to produce piezoelectric transformers having a voltage breakdown of about 50 kv/cm or more.

**PIEZOELECTRIC CERAMIC COMPOSITIONS
AND METHODS FOR PRODUCTION THEREOF**

BACKGROUND OF THE INVENTION

1. **Field of the Invention**

The present invention relates to piezoelectric (PZT) ceramic compositions. More particularly, it relates to low-loss PZT ceramic compositions cofirable with silver at a reduced sintering temperature and to methods for producing such compositions.

2. **Description of Related Art**

The low-temperature sintering of lead-based piezoelectric ceramics has been studied extensively by those in the electronic materials industry. For example, it has been found that through the addition of various frits, glass additives or softening agents, the sintering temperature of lead zirconate titanate (PZT) ceramics may be reduced from about 1250°C to about 960°C. Furthermore, it has been found that, in general, the sintering temperature of a lead based piezoelectric ceramic may be reduced by doping the piezoelectric composition with low-melting oxides.

Reference is made to an article titled "Low-Temperature Sintering of Lead-Based Piezoelectric Ceramics" by Gui Zhilun et al., Department of Chemical Engineering, Tsinghua University, Beijing, China (J. Am. Ceram. Soc., 72[3] 486-91 (1989)). This article discusses how to reduce the sintering temperature of a PZT composition by the addition of a small amount of a lower melting frit, B_2O_3 -- Bi_2O_3 -- CdO , while maintaining desirable electrical properties. Although this article discusses hard (low-loss) PZT ceramic materials, the sintering temperature is still too high for large scale manufacturing of PZT ceramics cofirable with a pure silver electrode material. As such, this composition may be of limited use in a large scale production environment.

U.S. Pat. No. 5,433,917 issued July 18, 1995 to Srivastava et al. teaches the manufacture of a morphotropic PZT ceramic composition having reduced sintering temperatures and a process for producing the same. In this patent, the PZT is sintered with an effective amount of an

eutectic mixture of copper oxide (CuO) and an oxide of an alkaline earth metal, preferably barium oxide and/or strontium oxide, to reduce the sintering temperature of the PZT composition to about 1000°C.

Although this patent discusses the addition of CuO as part of the frit, it deals primarily with soft-PZT materials which typically have high loss characteristics and are typically not intended for use in high power applications. This patent also addresses only a very narrow field of compositions, namely morphotropic lead zirconium titanate piezoelectric ceramic compositions, containing about 52(mole or atomic) % lead zirconate and 48(mole or atomic) % lead titanate.

It has been found that the compositions taught in the 5,433,917 patent are of limited use in the large scale manufacture of piezoelectric ceramic products such as piezoelectric multilayer transformers where low-loss properties accompanied by moderate coupling capabilities are desirable. In particular, a sintering temperature in the range of about 950°C still poses major cofiring problems with conventional silver (Ag) compositions, which typically have a melting temperature of about 962°C, and which are used to form the electrode patterns in standard multilayer packages. Potential problems during the sintering process may include, but are not limited to, silver-ceramic reactions at boundary layers, volatile silver vapor resulting in bubbles or trapped gases, uneven or incomplete shrinkage or densification, degradation of electrical properties, or delamination, all leading to possible product failure.

To combat these adverse effects of sintering so close to the melting point of Ag, many manufacturers have chosen to employ a silver-palladium (Ag-Pd) electrode composition. Ag-Pd compositions have a melting point which is dependent upon the Pd content in the composition. For example, a 90% Ag-10% Pd composition has a melting temperature of about 1020°C. This higher temperature processing can become very expensive compared to the processing costs associated with pure Ag electrode compositions. Higher sintering temperatures necessitate the

use of more expensive noble metals such as Pt, Pd, Au, or their alloys (which have higher melting points) as the internal electrode material. Thus, use of lower sintering temperature PZT materials may result in substantial savings in the cost of electrode materials as well as substantial savings in energy necessary for high temperature firing.

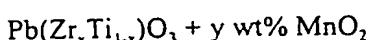
Commonly assigned, U.S. Patent No. 5,792,379, issued to the same inventors as the present application, discloses a low loss PZT composition capable of being cofired with a silver electrode layer at temperatures of about 900°C. The composition consists of a main composition and an additive, the main composition being PZT and the additive comprising a glass frit composed of a combination of B_2O_3 , Bi_2O_3 , and some other metal oxide (MeO). However, the composition disclosed in the 5,792,379 patent employs a glass frit additive that adds extra steps which involve the making of glass and cost to the production of the PZT composition. Thus, it would be desirable to provide a PZT composition that can be formulated without the use of a glass additive.

Another problem encountered with prior art compositions is that the low-melting additions, which decrease the sintering temperature, also may modify the properties of the ceramics, causing degradation of the electrical properties of the composition which render these compositions impractical for their intended purposes as low-loss devices.

SUMMARY OF THE INVENTION

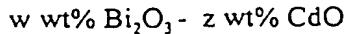
The present invention is direct to a glass-free piezoelectric ceramic composition comprising:

a first component represented by the general formula:



in which x is a mole percentage and y is a weight percentage and wherein x is within a range from 0.0 to about 1.0 mole or atomic %, and y is within a range from about 0.1 to about 1.0; and

a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0.

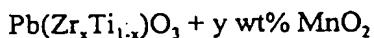
The present invention is also directed to method for producing piezoelectric ceramic compositions as described above. The present invention further includes a piezoelectric transformer formed from a piezoelectric ceramic composition as described above and a method for production thereof.

DETAILED DESCRIPTION

The piezoelectric ceramic composition of the present invention includes at least a first component and a second component.

The First Component

The first component is represented by the following formula:



in which x is a mole percentage and y is a weight percentage and wherein $0 \leq x < 1.0$ and $0.1 \leq y \leq 1.0$.

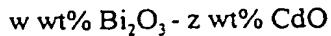
Manganese dioxide (MnO_2) is a known metal oxide dopant used to reduce the dielectric losses in PZT ceramic compositions. The addition of about 0.1 to 1.0 weight percent MnO_2 to the main composition of the first and second components is also known to promote densification as well as to enhance the mechanical quality factor (Q_m). The addition of a small amount of MnO_2 will increase Q_m . However, if too much MnO_2 is added to the main composition, then other electrical properties, such as the dielectric constant (k') or the coupling coefficients (K_t & K_p), may be reduced to an unacceptable level. Also, the amount of MnO_2 should not be less than 0.1 or Q_m will not be

sufficiently increased. Conversely, the amount of MnO_2 should not be greater than 1.0 weight percent or k' , K_r , and K_p may be decreased to unacceptable levels.

An important feature of this invention is the low-temperature sinterability of the composition, which is achieved through a predetermined and specially formulated additive, and which can be applied over the entire PZT diagram. Stated another way, the sintering additive can be incorporated with zirconium/titanium (Zr/Ti) compositions having molar ratios from 100% zirconium/0% titanium to 0% zirconium/100% titanium. The aforementioned compositional flexibility is significant because different piezoelectric compositions are often required for different applications. For example, a Rosen-Type piezoelectric transformer application may require a composition with a Zr/Ti ratio close to the morphotropic phase boundary. On the other hand, for a high power/low turns ratio application such as a multilayer-stack piezoelectric transformer, a higher relative percentage of PbTiO_3 as compared with PbZrO_3 could be utilized. There will be considerably more Ti than Zr in this composition. Nevertheless, by incorporating a predetermined amount of the second component into the composition, a low sintering temperature composition cofirable with pure Ag at about 900°C. is provided.

The Second Component

A second component is added to the first component to lower the sintering temperature while maintaining good electrical properties of the resultant composition. The second component is represented by the general formula:



in which w and z represent weight percentages and wherein $0.1 \leq w \leq 1.0$ and $0.1 \leq z \leq 2.0$.

The amount of the second component preferably ranges from 0.5 to 5.0 weight percent of the total composition of first and second components. Although more or less of the

second component may be added to the first component, certain disadvantages may occur. For example, if more than 5.0 weight percent is added, then the electrical properties of the PZT composition may be degraded. In addition, if less than 0.5 weight percent is added, there may be insufficient densification of the PZT composition at a sintering temperature of 900°C.

One ingredient in the second component is bismuth oxide. Bismuth oxide (Bi_2O_3) has a melting temperature of 825°C. Although not intending to be bound by theory, the significance of this component is realized at the atomic level. The ionic radii of Bi^{3+} and Bi^{5+} are 0.96 Å and 0.74 Å, respectively, comparing to that of Ti^{4+} (0.68 Å) and Zr^{4+} (0.79 Å). Replacement of Ti^{4+} and/or Zr^{4+} by Bi^{3+} and Bi^{5+} ions is believed to result in the constraining of domain walls in the PZT grain due to the larger ionic radius of the replacement ions. This is believed to have the effect of reducing both dielectric and mechanical losses.

The amount of the Bi_2O_3 in the second component preferably ranges from 0 to 0.80 weight percent of the weight of the second component. Although more Bi_2O_3 may be added, certain disadvantages may occur. For example, although not intending to be bound by theory, it is believed that if the content of the Bi_2O_3 exceeds 0.80, then the PZT may difficult to completely densify because it is postulated that the excess Bi_2O_3 exceeds the solubility limit of Bi into the PZT lattice structure in the given time domain of interest.

Another ingredient in the second component is CdO. CdO is added to the composition to reduce the sintering temperature and improve the loss characteristics (Q_m and $\tan \delta$). Although other additives are available to reduce the sintering temperature, CdO is preferred because it does not increase the electrical and mechanical losses as much as other additives.

Methods of Production

The following are Examples of preferred methods of preparing a piezoelectric ceramic composition according to the present invention.

EXAMPLE 1

A composition was prepared using PbO, ZrO₂, TiO₂, CdO, and MnO₂ as raw materials. A mixture with the proper amounts (the amounts depended on composition needed) of PbO, ZrO₂, TiO₂, CdO, and MnO₂ was wet-milled with a ball mill for 12 hours and then dried in an oven. The dried powder was then screened through a 40 mesh sieve and placed in an alumina crucible. Next, the powder was calcined at 850°- 900°C for 1-4 hours, then crushed and ground to prepare calcined powder having such a particle size that the particles could pass through a 100 mesh sieve.

Bi₂O₃ powder was added to the mixture and wet mixed in a vibratory mill for 12 to 16 hours until a particle size of 1 to 4 µm was achieved. The mixture was then dried in an oven. Next, 1-3 wt% polyvinyl alcohol and 0.5-1.5 wt% polyethylene glycol were added to the dried mixture. The mixture was formed into pellets using a uniaxial dry press at approximately 10,000 psi. Green, unfired pellets were then sintered at 900°C for 2-6 hours.

EXAMPLE 2

A composition was prepared using PbO, ZrO₂, TiO₂, and MnO₂ as raw materials. A mixture with the proper amounts (the amounts depended on composition needed) of PbO, ZrO₂, TiO₂, and MnO₂ was wet-milled with a ball mill for 12 hours and then dried in an oven. The dried powder was then screened through a 40 mesh sieve and placed in an alumina crucible. Next, the

powder was calcined at 850°- 900°C for 1-4 hours, then crushed and ground to prepare calcined powder having such a particle size that the particles could pass through a 100 mesh sieve.

Bi_2O_3 and CdO powders were added to the mixture and wet mixed in a vibratory mill for 12 to 16 hours until a particle size of 1 to 4 μm was achieved. The mixture was then dried in an oven. Next, 1-3 wt% polyvinyl alcohol and 0.5-1.5 wt% polyethylene glycol were added to the dried mixture. The mixture was formed into pellets using a uniaxial dry press at approximately 10,000 psi. Green, unfired pellets were then sintered at 900°C for 3-6 hours.

Properties

The properties of several examples of the piezoelectric ceramic compositions of the present invention were measured. The density of the sintered pellets was determined by the Archimedes method. The fired pellets were sliced to a thickness of approximately 0.4 mm and sputtered with gold (Edwards S150B) to form electrodes thereon. The electroded discs were then poled at 120°C at an electric field 25-40 kV/cm for 5-10 minutes. The coupling coefficient (d_{33}) was measured using a Berlincourt meter to assure the samples were properly poled.

Measurement was performed on a computer-controlled Hewlett-Packard 4194A Impedance/Gain-Phase Analyzer. The measured parameters were: dielectric constant (k'), dielectric loss factor ($\tan \delta$), mechanical quality factor (Q_m), relative permittivity (ϵ) ($\epsilon = k' \cdot l \approx k'$) thickness coupling coefficient (K_c), planar coupling coefficient (K_p), as well as density (measured in g/cm^3). These experimental results are provided in the following TABLE 1.

TABLE I

Properties of $\text{Pb}(\text{Zr}_{0.55}\text{Ti}_{0.45})\text{O}_3 + 0.3 \text{ wt\% MnO}_2$, sintered at 900°C for 4 hours, poled at 25 kV/cm with sintering additives.							
Additive	Additive Amount	Density (g/cm³)	Q_m	k' (1 kHz)	$\tan \delta$ (%)	K_p	K_t
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/0.05wt%	7.63	360	400	0.54	0.45	0.44
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/0.10wt%	7.71	430	400	0.62	0.45	0.44
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/0.25wt%	7.85	420	490	0.53	0.47	0.45
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/0.50wt%	7.85	420	510	0.51	0.46	0.45
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/0.75wt%	7.83	500	530	0.58	0.45	0.44
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/1.0wt%	7.83	500	540	0.49	0.45	0.44
$\text{Bi}_2\text{O}_3/\text{CdO}$	0.5wt%/1.5wt%	7.77	660	560	0.55	0.36	0.36
$\text{B}_2\text{O}_3\text{-}\text{Bi}_2\text{O}_3\text{-}\text{CdO}$ (glass) (prior art)	2 wt%	7.81	500	440	0.23	0.44	0.46

Piezoelectric ceramic materials are known to have a perovskite crystal lattice structure. A generic perovskite crystal structure is shown by the general formula $A^{2+}B^{4+}\text{O}_3$. The selection of certain materials in the formulation of these compositions results in changes to the crystal structure during sintering. For example, the incorporation of Bi results in Bi^{3+} ions on the A-site and Bi^{3+} and Bi^{5+} ions on the B-site of the perovskite structured PZT. This results in improved properties during sintering.

Another feature of the compositions of the present inventions are that the sintering additives can be incorporated directly into the PZT lattice to enhance certain electric and piezoelectric properties of the PZT composition. For example, a relatively high dielectric constant, high mechanical quality factor (Q_m), relatively high coupling factors and low dielectric loss properties may all be desirable for applications such as a piezoelectric transformer.

In one preferred embodiment of the present invention, the piezoelectric ceramic composition will be particularly suited for high-power, high-voltage piezoelectric applications. The

desirable electrical properties include a low mechanical loss Q_m of about 400 or more, a k' of 500 or more a planar coupling coefficient K_p of about 0.35 or more, a thickness coupling coefficient K_t of about 0.40 or more, a density of about 7.4 g/cm^3 or more, a dielectric constant k' value of about 600 or more, and a $\tan \delta$ factor of about 1% or less.

The compositions of the present invention may be achieved by a conventional mixed-oxide process. Those skilled in the art will understand this to mean that various oxide powders are mixed, calcined, and fired to achieve a composition with the desired properties.

The internal electrodes of typical high-temperature fire multilayer piezoelectric devices typically comprise a silver palladium alloy, most preferably a 70% silver/30% palladium alloy or a 90% silver/10% palladium alloy. An important feature of the compositions of the present inventions are that they are custom formulated such that they can be used with a pure silver paste.

In summary, the present invention provides PZT ceramic compositions which are cofirable with silver at a reduced sintering temperature of 900°C or less without the use of a glass additive, and which are non-reactive with a silver electrode layer when cofired therewith. The compositions of the present invention can be fully densified at low temperatures, and can maintain desired electrical properties of a low-loss PZT while also being adaptable to large scale manufacturing processes. The piezoelectric compositions may be further processed to produce specific components such as a multilayered ceramic transformer device, for example. The piezoelectric ceramic compositions may be cofired with silver electrode layers at a temperature of about 900°C and, due to the properties of the compositions, the electrode layers are non-reactive with the piezoelectric ceramic compositions. One typical application for the present piezoelectric ceramic compositions may be as piezoelectric transformers used in a high voltage application wherein the voltage breakdown is about 50 kv/cm or more.

Although various embodiments of this invention have been shown and described, it

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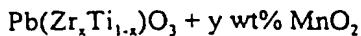
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should be understood that various modifications and substitutions, as well as rearrangements and combinations of the preceding embodiments, can be made by those skilled in the art, without departing from the novel spirit and scope of this invention.

WHAT WE CLAIM IS

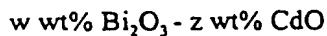
1. A piezoelectric ceramic composition comprising:

a first component represented by the general formula:



in which x is a mole percentage and y is a weight percentage and wherein x is within a range from 0.0 to about 1.0, and y is within a range from about 0.1 to about 1.0; and

a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0.

2. The piezoelectric ceramic composition according to claim 1, wherein the piezoelectric ceramic composition is nonreactive with a silver electrode layer when cofired therewith at sintering temperatures of about 900°C.

3. The piezoelectric ceramic composition according to claim 1, wherein the piezoelectric ceramic composition is a hard PZT ceramic.

4. The piezoelectric ceramic composition according to claim 1, wherein said first component is present in the composition at a weight percent ranging from about 95 to about 99.5 weight percent and said second component is present in the composition at a weight percent ranging from about 0.5 to about 5 weight percent.

5. The piezoelectric ceramic composition according to claim 1, wherein the piezoelectric ceramic composition is produced by a mixed-oxide process.

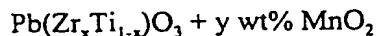
6. The piezoelectric ceramic composition according to claim 1, wherein said second component is glass-free.

7. The piezoelectric ceramic composition according to claim 1, wherein the piezoelectric ceramic composition has the following properties:

mechanical loss (Q_m) of about 400 or greater;
(k') of 500 or more;
planar coupling coefficient (K_t) of about 0.35 or greater;
thickness coupling coefficient (K_p) of about 0.40 or greater;
density of 7.4 g/cm³ or greater;
dielectric constant (k') of about 600 or greater; and
 $\tan \delta$ of about 1% or less.

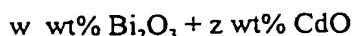
8. A piezoelectric ceramic composition comprising:

a first component represented by the general formula:



in which x mole percentage and represent y weight percentages and wherein x is .55 or 55% and y is .3%;

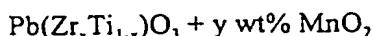
a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is 0.5% and z is 1.5%.

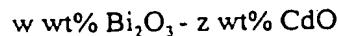
9. A piezoelectric transformer having a voltage breakdown of about 50 kv/cm or more produced from a piezoelectric ceramic composition comprising:

a first component represented by the general formula:



in which x is a mole percentage and y is a weight percentage and wherein x is within a range from 0.0 to about 1.0, and with y being within a range from about 0.1 to about 1.0; and

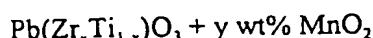
a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0.

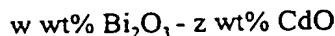
10. A method of making a piezoelectric ceramic composition comprising:

a first component represented by the general formula:



in which x is a mole percentage and y is a weight and wherein x is within a range from 0.0 to about 1.0, and y is within a range from about 0.1 to about 1.0; and

a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0, the method comprising the steps of:

preparing a mixture by first mixing PbO, ZrO₂, TiO₂, CdO, and MnO₂ in amounts corresponding to the above weight percentages;

wet-milling the mixture with a ball mill for 12 hours;

drying the mixture in an oven;

screening the mixture through a 40-mesh sieve.

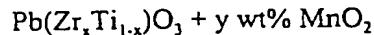
calcining the mixture at 850°-900°C for 1-4 hours;

pulverizing the mixture so that the resulting powder has a particle size capable of passing through a 100 mesh sieve;

adding Bi₂O₃ to the mixture in an amount corresponding to the above weight percentages in a wet-mill vibration mill for 12-16 hours to form a second mixture;

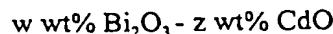
drying the second mixture; and
sintering the second mixture at 900°C for 2-6 hours.

11. A method of making a piezoelectric ceramic composition comprising:
a first component represented by the general formula:



in which x is a mole percentage and y is a weight percentage and wherein x is within a range from 0.0 to about 1.0, and y is within a range from about 0.1 to about 1.0; and

a second component represented by the general formula:



in which w and z represent weight percentages and wherein w is within a range from about 0.1 to about 1.0, and z is within a range from about 0.1 to about 2.0, the method comprising the steps of:

preparing a mixture by first mixing PbO, ZrO₂, TiO₂, and MnO₂;

wet-milling the mixture with a ball mill for 12 hours;

drying the mixture in an oven;

screening the mixture through a 40-mesh sieve.

calcining the mixture at 850°-900°C for 1-4 hours;

pulverizing the mixture so that the resulting powder has a particle size capable of passing through a 100 mesh sieve;

adding Bi₂O₃ and CdO to the mixture in a wet-mill vibration mill for 12-16 hours to form a second mixture;

drying the second mixture; and

sintering the second mixture at 900°C for 2-6 hours.

INTERNATIONAL SEARCH REPORT

Int'l Application No
 PCT/US 00/25903

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C04B35/491 H01L41/187

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC 7 C04B H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, COMPENDEX, INSPEC, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GUI ZHILUN ET AL: "Low-temperature sintering of lead-based piezoelectric ceramics" JOURNAL OF THE AMERICAN CERAMIC SOCIETY, MARCH 1989, USA, vol. 72, no. 3, pages 486-491, XP002156332 ISSN: 0002-7820 cited in the application	1-5,7-9
A	abstract page 486, right-hand column, paragraph 2 page 491, left-hand column, paragraph 5 table I	10,11

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

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Date of the actual completion of the International search

28 December 2000

Date of mailing of the international search report

16/01/2001

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
 NL - 2280 HV Rijswijk
 Tel: (+31-70) 340-2040, Tx. 31 651 epo nl.
 Fax: (+31-70) 340-3016

Authorized officer

Rosenberger, J

